

Electrodeposition mechanism of PbSe and PbTe epitaxial films on InP single crystals

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The lead chalcogenide narrow-gap semiconductors PbS, PbSe, PbTe have been applied in infrared detectors and thermal photovoltaic energy converters. The production of photonic devices implies an heteroepitaxial growth on Si or III-V semiconductors. We showed recently that PbSe can be epitaxially electrodeposited on InP single crystals thanks to the addition of Cd^{2+} in the electrolyte (1). In this study the growth mechanism of PbSe and PbTe films, epitaxied on $(\bar{1}\bar{1}\bar{1})$ InP, is examined.

PbSe and PbTe were electrodeposited using acidic solutions (0.1M HNO_3) containing 0.05 M $\text{Pb}(\text{NO}_3)_2$, 0.001 M SeO_2 or TeO_2 ; 0.5 M of $\text{Cd}(\text{NO}_3)_2$ is added in order to obtain epitaxial electrodeposits. PbSe and PbTe were electrodeposited on the P face $(\bar{1}\bar{1}\bar{1})$ of InP single crystals. Prior deposition, surfaces were etched 15s in a bromine(0.4%)-methanol mixture.

RHEED observations show that the best conditions of epitaxy are obtained when the cathodic potential is maintained at the beginning of the current plateau (-0.75V/SSE). Figure 1 shows a good epitaxy of PbSe; on the contrary PbTe (Figure 2) only presents a poor epitaxy probably related to a large lattice mismatch between InP and PbTe (9%). It has been showed that underpotential deposition (UPD) of Pb and Cd takes place on PbSe (2). We found (Figure 3) similar Pb and Cd UPD on InP single crystals indicating strong substrate-deposit interactions. The cadmium adsorption provokes an inhibition of superficial sites and a decrease of the PbSe electrodeposition current. Another consequence is the incorporation of Cd (1%) in the electrodeposits as determined by RBS. Local determinations on electrodeposits cross sections, by X ray dispersive energy analysis, using an electronic probe (diameter 1 nm), reveal an enrichment (2-4%) of Cd near the interface PbSe/InP. XPS measurements confirm the presence of Cd in the bulk and its enrichment at the PbSe/InP interface which is free of oxide or hydroxide. These results could be explained by the initial formation of a CdSe layer easily epitaxied on InP. As PbSe presents a small mismatch with CdSe (0.7%) its epitaxial growth is facilitated. The Cd concentration is maintained at a low level by a chemical displacement of Cd^0 by Pb^{2+} , considering the standard redox potentials of $\text{Cd}^{0/2+}$ (-1.06V/SSE) and $\text{Pb}^{0/2+}$ (-0.79V/SSE) reactions.

(1) L. Beaunier, H. Cachet, R. Cortes, M. Froment, Electrochemistry Communications 2, 2000, 508

(2) E.A. Streltsov, N.P. Osipovich, L.S. Ivaskevich, A.S. Lyakhov, Electrochimica Acta 44 1999, 2645

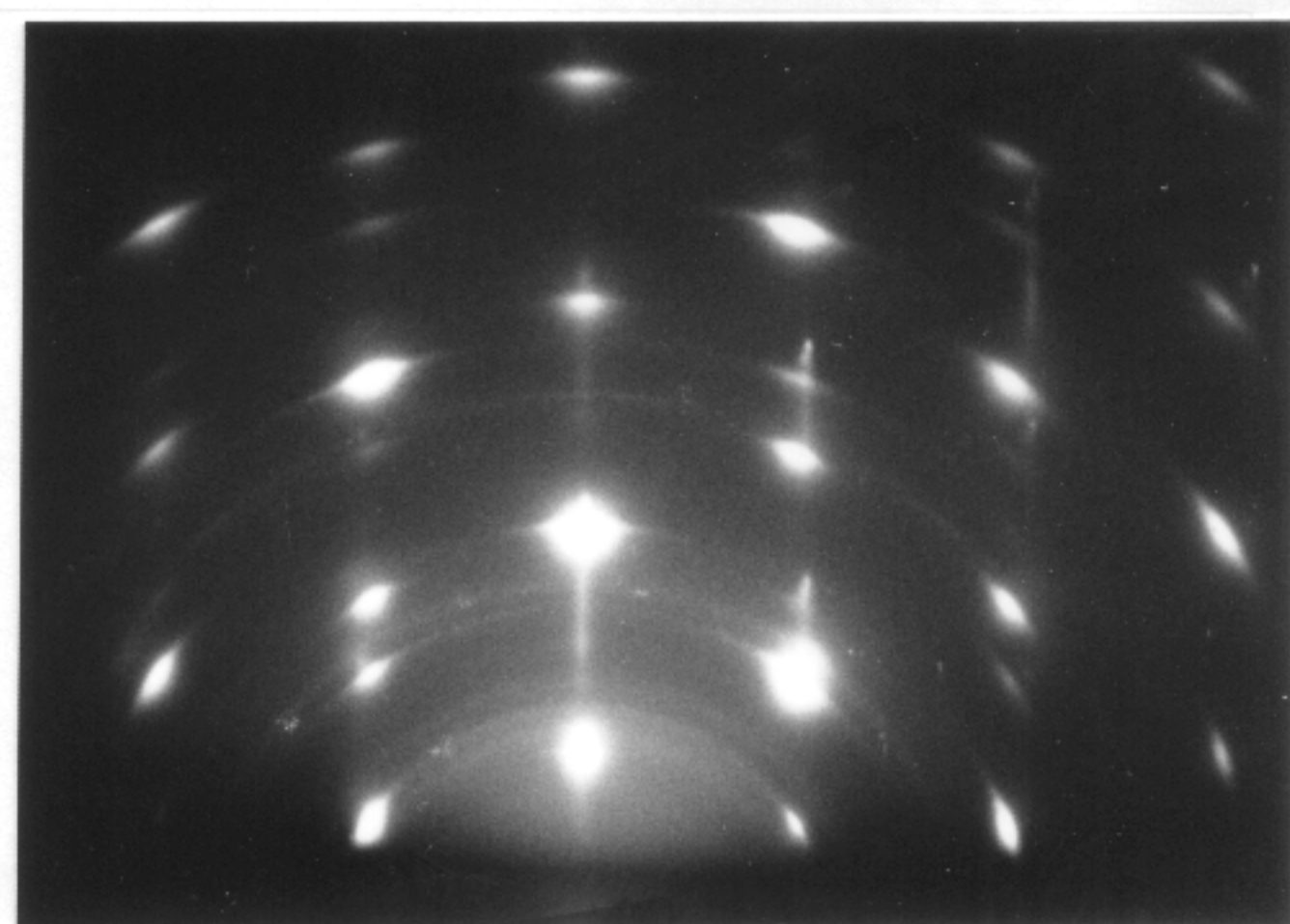


Fig.1: RHEED pattern of an epitaxial PbSe film (thickness: 180 nm) electrodeposited on (111) InP; observation in the $\langle 112 \rangle$ azimuth.

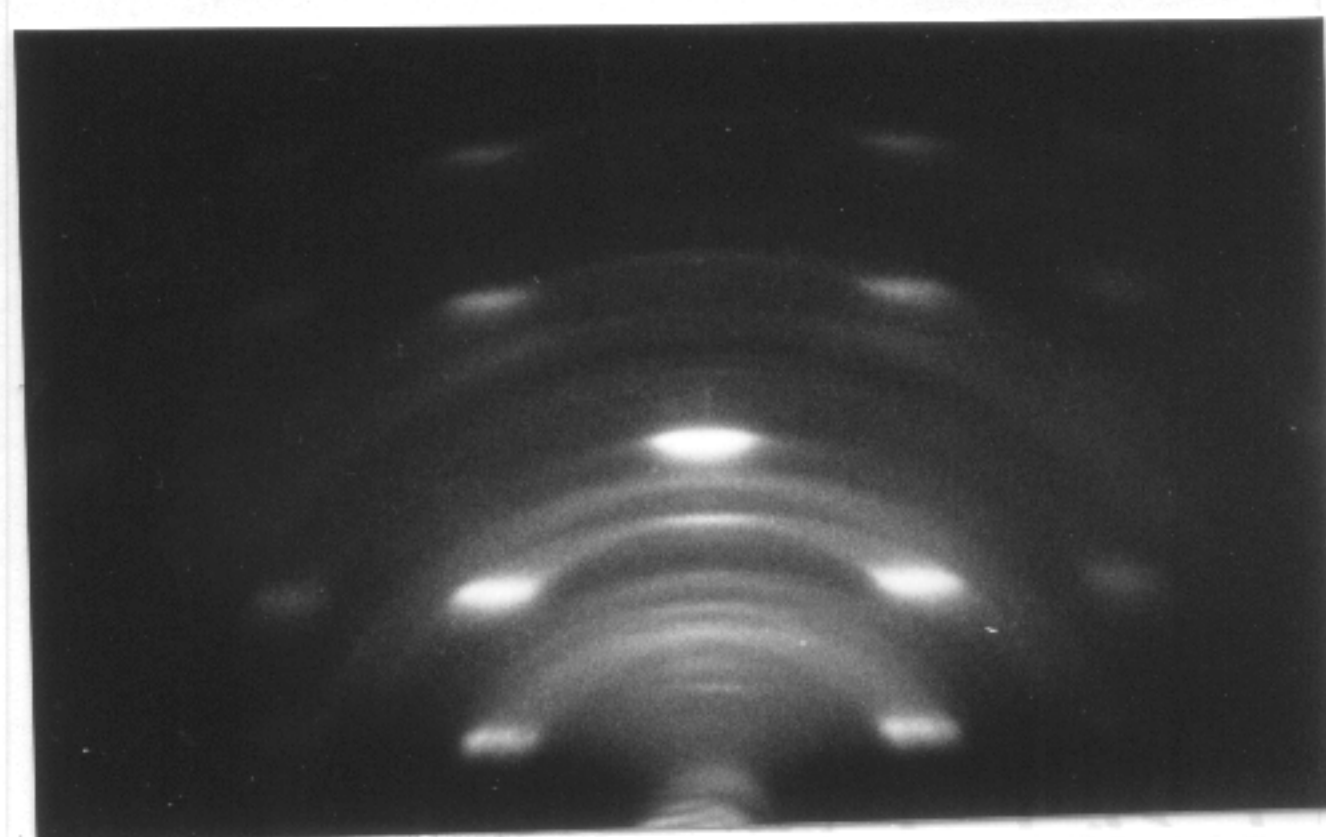


Fig.2: RHEED pattern of an epitaxial PbTe film (thickness: 50 nm); observation in the $\langle 011 \rangle$ azimuth; presence of polycrystalline material.

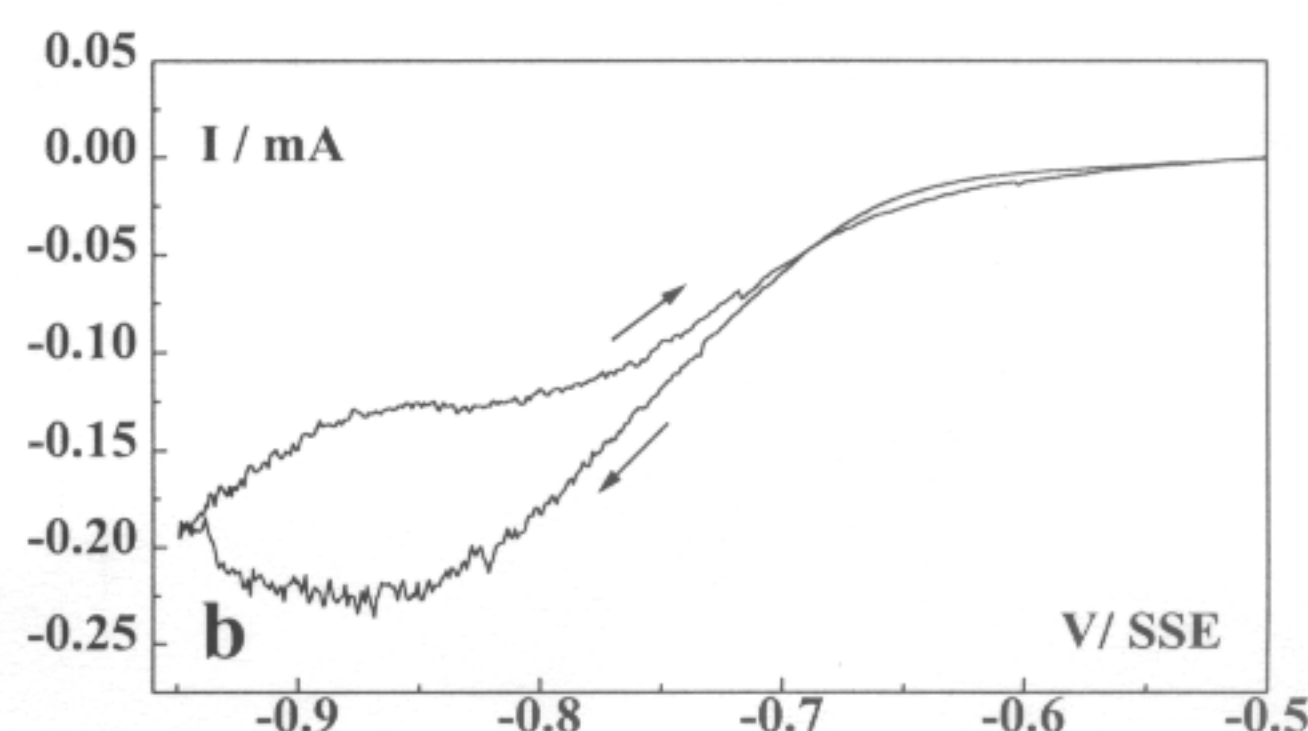
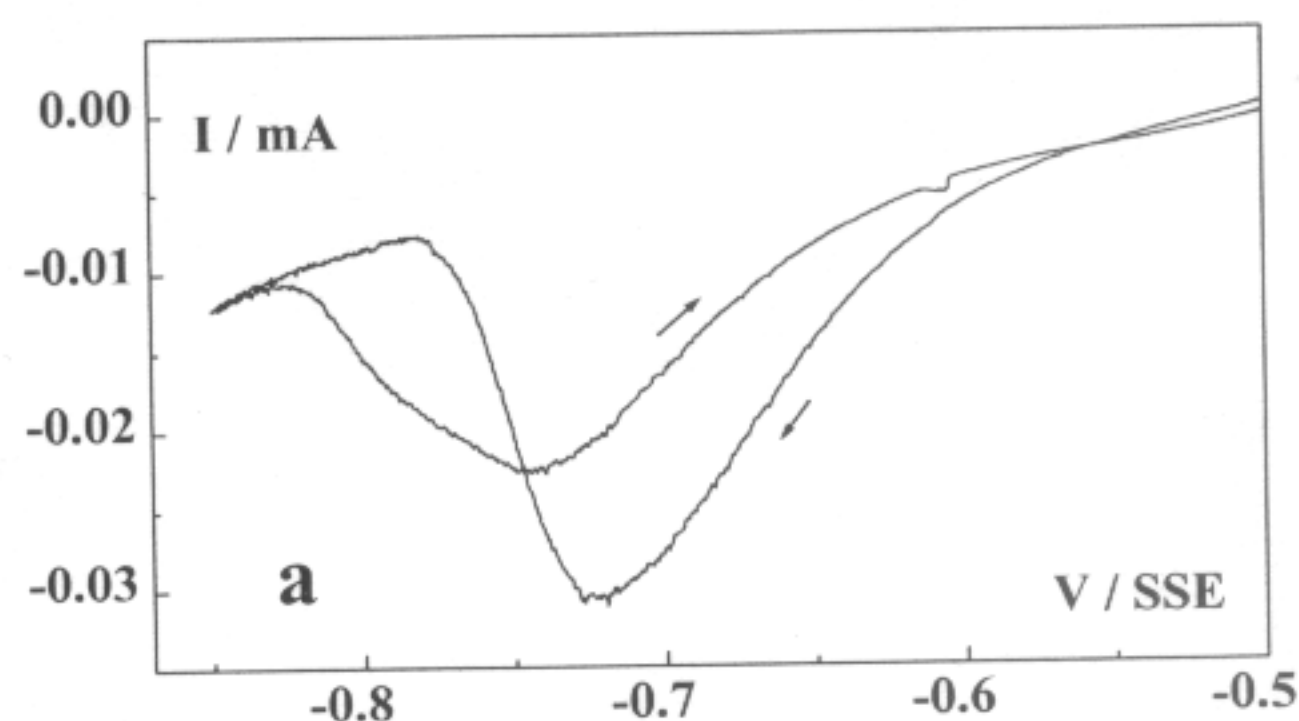


Fig.3: Current-potential curves for underpotential deposition of Pb (Fig.3a) and Cd (Fig.3b) on (111) InP substrates in 0.5 M HNO_3 with 0.001 M $\text{Pb}(\text{NO}_3)_2$ or $\text{Cd}(\text{NO}_3)_2$. Scan rate = 2 mV/s.